

Sorption–Desorption Behavior of Atrazine on Soils Subjected to Different Organic Long-Term Amendments

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Sorption of atrazine on soils subjected to three different organic amendments was measured using a batch equilibrium technique. A higher K_F value ($2.20 \text{ kg}^{-1}(\text{mg L}^{-1})^{-N}$) was obtained for soil fertilized with compost, which had a higher organic matter (OM) content. A correlation between the K_{FOC} values and the percentage of aromatic carbon in OM was observed. The highest K_{FOC} value was obtained for the soil with the highest aromatic content. Higher aromatic content results in higher hydrophobicity of OM, and hydrophobic interactions play a key role in binding of atrazine. On the other hand, the soil amended with farmyard manure had a higher content of carboxylic units, which could be responsible for hydrogen bonding between atrazine and OM. Dominance of hydrogen bonds compared to hydrophobic interactions can be responsible for the lower desorption capacity observed with the farmyard manure soil. The stronger hydrogen bonding can reduce the leaching of atrazine into drinking water resources and runoff to rivers and other surface waters.

KEYWORDS: Capillary electrophoresis; atrazine; sorption; soil

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) is a weak-base herbicide with a $\text{p}K_a$ of 1.7 used to control annual grasses and broadleaf weeds primarily in corn and sorghum (1, 2). Even though this herbicide has been banned in some countries, due to its resistance to chemical and biological degradation and is, therefore, accumulated in the environment (3), the application is yet allowed in many countries to control weeds (4). As a result of its extensive use, atrazine and metabolites have been detected at alarmingly high concentrations in soils, groundwaters, rivers, and lakes (3), being one of the most important pollutants of groundwater in many countries (5). Directive 98/83/EC has set the maximum concentration of atrazine to $0.1 \mu\text{g/L}$ and the total concentration for all pesticides to $0.5 \mu\text{g/L}$ in regard to quality of water for human consumption (6). The effects of atrazine on human health have been reported to induce increased risk of cancer in humans, although these conclusions are still controversial (6).

The transport and fate of hydrophobic organic contaminants in the environment involve complex phenomena that are influenced by many processes, including sorption to soil components, uptake by plants, transport via runoff and leaching, biodegradation, photodegradation, volatilization, and chemical degradation (7, 8). However, adsorption is one of the most important

processes that affect the fate of pesticides in soils and control their distribution in the soil/water environment (9). For the direct measurement of the adsorption coefficient of an organic molecule in soils the batch slurry method is generally used, which is based on OECD guideline 106 (10). The sorption interactions of pesticides may involve either mineral or organic soil components, or even both (11). It is widely accepted that organic matter plays the major role in the sorption phenomena of organic chemicals in soils, mainly for relatively nonpolar substances, such as atrazine (6, 8). However, the contribution of the inorganic soil components, particularly the clay fraction, is also significant, especially in soils containing low organic matter contents (11). Whereas Sparks and Swift (11) assume that the total organic matter content is more important for sorption processes than the composition of the organic matter, Kulikova and Perminova (12) reported that the extent of atrazine sorption to humic substances was strongly correlated to the aromaticity of the organic matter. Desorption of chemicals is also critical as it determines the availability of the species, their release rate into runoff and the risk for groundwater pollution (13, 14). The degree of reversibility in adsorption–desorption reactions is of importance for the evaluation of the mobility of pesticides, and several studies have indicated the occurrence of hysteresis (7, 14). However, the exact mechanism of hysteretic adsorption/desorption remains largely unknown, but it is suggested that sorption of pesticides occurs with a limited degree of reversibility depending on the

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Table 1. Influence of Long-Term Application of Different Organic Fertilizers and Mineral Fertilizer, Respectively, on Chemical Soil Parameters and Relative Area Distribution (Percent of Total Spectrum Area) of Solid-State ^{13}C CPMAS-NMR Spectra (17)

soil	pH	TN ^a (%)	TOC ^b (%)	chemical shift region (ppm)								
				alkyl	O,N-alkyl				aromatic			carboxyl
				R1 0–45	R2 45–110	R2a 45–60	R2b 60–90	R2c 90–110	R3 110–160	R3a 110–140	R3b 140–160	R4 160–190
SLU	6.5	0.151	1.983	29.9	44.2	11.6	26.6	6.0	16.7	12.5	4.2	9.3
FYM	6.2	0.131	1.473	26.2	41.5	10.8	23.6	7.1	21.5	16.5	5.0	10.8
COM	7.1	0.227	2.775	37.4	44.4	13.0	26.3	5.2	12.6	10.4	2.2	5.6
MIN	6.1	0.109	1.238	30.4	43.7	10.8	24.7	8.1	20.2	15.1	5.1	5.7

^aTotal nitrogen. ^bTotal organic carbon.

physical–chemical properties of the molecules and soils involved (14). It is usually explained by irreversible chemical binding, sequestration of a solute into specific components of the solid organic matter, or entrapment of the solute into microporous structures or into the solid organic matter matrix (15).

A large number of studies dealt with the interaction between atrazine and soil organic matter; however, the binding mechanism is still a subject of controversial discussions. Between the different mechanisms proposed, only some are generally accepted. According to Spark and Swift (11) atrazine has functional groups capable of engaging H-bonding, van der Waals bonding, and ligand exchange. The carboxylic and phenolic functional groups of organic matter are considered by Chefetz et al. (15) to play an important role in the sorption interaction by H-bonding. They suggest that the sorption mechanism of atrazine comprises both nonspecific (hydrophobic interactions with aromatic and/or aliphatic domains) and specific (H-bonding to carboxylic and phenolic groups) interactions. Celano et al. (3) are in favor of a charge-transfer mechanism at pH < 4.5; however, such conditions are not environmentally relevant and also refer to the existence of a predominant role of weak dispersive forces. Kulikova and Perminova (12) considered hydrophobic binding to be the key interaction underlying the binding of atrazine to humic substances. Boivin et al. (14) also refers to hydrophobic interactions on weak energetic sites to explain the binding mechanism.

During the past years numerous investigations were made to understand the sorption phenomena of atrazine to soils. In the majority of these works different soil and sediment samples, with different organic and mineral characteristics, were used (13–16). Although herbicide sorption in soils has been extensively studied throughout the world, in our work we compared a soil sample subjected to a mineral and three different organic fertilizations for more than 45 years. The structural characterization of soil organic matter, which will be used to perform the adsorption/desorption experiments, was previously reported (17). The aim of our study was to evaluate the effects of soil organic matter (SOM) with different structural characteristics in the atrazine sorption behavior using a batch equilibrium assay. We expect that the results can increase our understanding of the mechanism of the sorption phenomena by revealing the types of interactions present. This understanding can be important knowledge in the use of organic fertilizations to control the fate of atrazine in the soil environment and its bioavailability, as well as leaching into groundwater.

MATERIALS AND METHODS

Soil Samples. Soil samples (0–30 cm) were collected, 30 months after the last application of the organic fertilizers, from a long-term field experiment that was established in 1962 at the experimental farm of INRES-Institute of Plant Nutrition, University of Bonn, on a luvisol derived from loess (17.8% clay, 67.3% silt, 5.9% sand),

following a cereal-root crop sequence (18). The treatments selected for the present investigations were sewage sludge from municipal wastewater treatment facilities (14.88 t ha^{-1}) (SLU), farmyard manure (9 t ha^{-1}) (FYM), compost from organic household waste (58 t ha^{-1}) (COM), and mineral fertilizer (MIN). We cannot present the most relevant properties of the substrates used as fertilizers due to the long time of the amendments experiments—40 years. However, the soil samples used in this study were characterized previously using different analytical techniques (17), and a summary of the chemical soil properties and relative area distribution (percent of total spectrum area) of solid-state ^{13}C CPMAS-NMR spectra is presented in Table 1.

Instrumentation. All measurements were performed using a Beckman P/ACE MDQ capillary electrophoresis (CE) system equipped with a diode array detector (DAD). Separation was carried out on an uncoated fused silica capillary of 60 cm total length (50 cm effective length to the detector), 75 μm internal diameter and 375 μm external diameter.

Buffer and Standards. The run buffer was prepared weekly with 10 mM of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (99%, Fluka) and 25 mM sodium dodecyl sulfate (SDS) (99%, Panreac) in ultrapure water, obtained from a Milli-Q (Millipore Q plus 185) system; pH was adjusted to 8.56 ± 0.02 with 1 M NaOH. A stock of internal standard (IS) solution, ethylvanillin (99%, Aldrich), was prepared at a concentration of 1670 mg/L by dissolving in a small quantity of acetonitrile and filling the volumetric flask with ultrapure water. A stock standard solution of atrazine (97.4%, Riedel-de Haën) was prepared in methanol. Standard solutions were prepared, from stock solution, to obtain a final concentration ranging from 0.3 to 10 mg/L. All of the dilutions were made using a 0.01 M solution of CaCl_2 to have the same concentration of CaCl_2 present in the samples. The IS was added to the standards and samples to obtain a final concentration of 1.67 mg/L before analysis. Buffer, standards, and samples were filtered through a 0.22 μm filter (Millex-GV from Millipore) before analysis.

Capillary Column Conditioning. New capillaries were conditioned with 1 M NaOH for 7 min, followed by 60 min, with 0.1 M NaOH, 5 min with ultrapure water, and finally 5 min with electrolyte. The capillary was conditioned every day with 1 M NaOH, 0.1 M NaOH, ultrapure water, and electrolyte for 5 min each to obtain a stable baseline and to improve the reproducibility of the migration time. Before each injection, the capillary was flushed with 0.1 M NaOH for 3 min, ultrapure water for 2 min, and electrolyte for 3 min. All flushing was performed using 20.0 psi pressure.

Separation and Detection Conditions. The injections of standards and samples were made using 0.5 psi pressure during 3 s. Electrophoretic separations were carried out at a positive power supply of 20 kV for 7 min, maintaining the capillary temperature at 25 °C, resulting in a current of $\sim 60 \mu\text{A}$.

Atrazine and ethylvanillin were monitored by detection at 214 nm or in the range of 190–600 nm for multiwavelength detection. The run buffer vials were used for six consecutive injections before replacement with new vials.

Adsorption Studies. Adsorption isotherms of atrazine were set up using the batch equilibration technique (10). Five pesticide concentrations were prepared in 0.01 M calcium chloride ranging between 2 and 10 mg/L. An aliquot of each concentration of atrazine solution was added to soil to obtain a final 1:2 soil/solution ratio. Five adsorption experiments were made for each concentration. The tubes were shaken in a head-over-head shaker for 24 h at 20 ± 1 °C. According to previous kinetic studies, equilibrium was assumed to be reached within the 8 h equilibration period

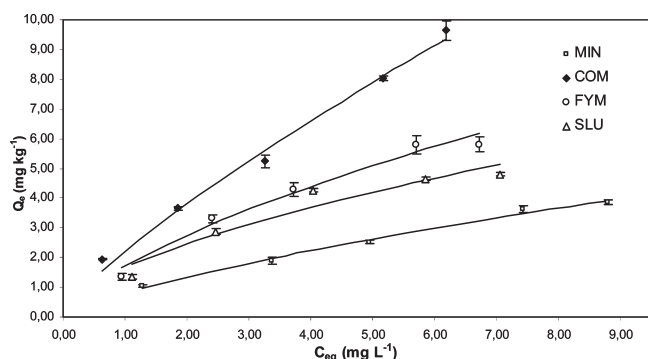


Figure 1. Freundlich adsorption isotherms for atrazine in soils subjected to different fertilizations (MIN, mineral fertilizer; COM, compost fertilizer; FYM, farmyard manure; SLU, sewage sludge fertilizer; error bars represent 95% confidence interval for $n = 3$).

(data not shown). Samples were then centrifuged at 1680g for 20 min, and aliquots of 3 mL of the supernatants were filtered and analyzed by capillary electrophoresis, using ethylvanillin as the IS. Previous studies have indicated that degradation and adsorption of atrazine to the test tubes can be ignored during the period of our study (19).

The amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentrations in solution. The initial concentration was considered to be the amount of atrazine present in the controls (without soil). Sorption isotherms were obtained by plotting the amount of atrazine sorbed per unit weight of soil at equilibrium (Q_e , mg kg^{-1}) versus the amount of chemical per volume of solution at equilibrium (C_e , mg L^{-1}).

Desorption Studies. These experiments were conducted immediately after the sorption experiments, and the supernatant was removed to leave only 25% of the original volume of solution in the vessel. The solution in the vessel was then made up to the original volume with 0.01 M CaCl_2 , after which the tubes were shaken at $20 \pm 1^\circ\text{C}$ for 24 h and centrifuged at 1680g for 20 min and the supernatant was again analyzed. This procedure was repeated until the concentration of atrazine in solution was above the detection limit of the analysis method. The lower concentration of adsorption was not used for desorption study because the concentrations expected were lower than the limit of detection of the method.

Data Analysis. The Freundlich parameters (K_F and N) were calculated from the fitting of nonlinear regression of the equation $Q_e = K_F \times C_e^N$, to the experimental data, where Q_e is the total sorbed concentration (mg kg^{-1}), C_e is the solution-phase concentration (mg L^{-1}), K_F ($\text{mg kg}^{-1}(\text{mg L}^{-1})^{-N}$) is the Freundlich distribution coefficient, and N is the isotherm nonlinearity factor. Isotherms were plotted (Q_e vs C_e), and K_F and N were obtained after the nonlinear regression had been performed. The K_F values were normalized to the organic carbon (OC) content of the soil to obtain $K_{F\text{OC}}$. Desorption isotherms were obtained and $K_{F\text{des}}$ and N_{des} calculated. The $K_{F\text{des}}$ values were normalized to the organic carbon (OC) content of the soil to obtain $K_{F\text{OCdes}}$. The ratios of the Freundlich exponents for desorption and sorption (N_{des}/N) were calculated and used as the desorption apparent hysteresis index (AHI). Lower index values indicate increased difficulty of the sorbed analyte to be desorbed from the matrix (15, 20).

RESULTS AND DISCUSSION

Adsorption Studies. Adsorption isotherms, obtained by plotting the amount of atrazine sorbed per unit weight of soil at equilibrium (Q_e , mg kg^{-1}) versus the amount of chemical per volume of solution at equilibrium (C_e , mg L^{-1}), are shown in Figure 1.

The Freundlich equation has reasonably described the adsorption of atrazine on the soil samples used, with correlation coefficients ranging from 0.934, for soil fertilized with sewage sludge, to 0.991, for mineral soil (Table 2). The Freundlich adsorption coefficient is an empirical constant of the Freundlich model expressing soil sorbent capacity (sorption isotherm slope)

Table 2. Parameters of the Freundlich Equation Describing the Adsorption Isotherms of Atrazine to the Four Soil Samples Used

soil ^a	K_F^b	N^b	$K_{F\text{OC}}^b$	R^2
MIN	0.81 (0.08)	0.72 (0.05)	65.5 (6.5)	0.991
SLU	1.67 (0.31)	0.57 (0.11)	84.2 (15.6)	0.934
FYM	1.73 (0.23)	0.67 (0.08)	117.3 (15.7)	0.974
COM	2.20 (0.22)	0.79 (0.06)	79.17 (7.9)	0.990

^a MIN, mineral fertilizer; SLU, sewage sludge fertilizer; FYM, farmyard manure; COM, compost fertilizer. ^b Standard deviation of the evaluated value is on parentheses.

Table 3. Correlation Coefficients (r) between the Parameter K_F or $K_{F\text{OC}}$ and TOC or Relative Area Distribution (Percent of Total Spectrum Area) of Solid-State ^{13}C CPMAS-NMR Spectra

	TOC	alkyl	O,N-alkyl	aromatic	carboxyl
correlation coefficient (r)	0.936 ^a	-0.583 ^b	-0.842 ^b	0.397 ^b	0.869 ^b

^a Correlation using K_F . ^b Correlation using $K_{F\text{OC}}$.

for a given range of atrazine concentration (14). A high K_F value reflects high adsorption capacity and is commonly associated with lower permeability of soils and thus lower leaching potential (5). The highest K_F value, $2.20 (\text{mg kg}^{-1} (\text{mg L}^{-1})^{-N})$, among the four soils samples used in this study was observed for the adsorption of atrazine on soil fertilized with compost, which presented simultaneously the highest organic carbon (2.775%) and nitrogen (0.151%) contents. In contrast, the lowest K_F value ($0.81 (\text{mg kg}^{-1} (\text{mg L}^{-1})^{-N})$) was found in soil fertilized with mineral salts only, having resulted—over the long-term application period—in low organic carbon (1.238%) and nitrogen (0.109%) contents. The correlation coefficient (r) between K_F values and total organic carbon was calculated (Table 3), and based on the results it is possible to verify a positive correlation between organic carbon content and soil sorption capacity. However, because FYM soil with 1.473% of organic carbon content presented a slightly higher K_F value than SLU soil, with 1.983% organic carbon, we presume that the Freundlich adsorption constant not only can be correlated with the soil organic carbon content but must also be correlated with the different functional groups. Singh et al. (21) evaluated the correlation between K_F and relative structural carbon percentage of SOM fractions. However, Singh et al. (21) used other pollutants, and the SOM was constituted only by humic acids, humin and lignin. In our study complete soil samples were used, and no correlation was found between K_F and different functional groups content. Because we observed a strong correlation between total organic carbon (TOC) and K_F that could disguise the real influence of organic matter characteristics, it is important to use the K_F value normalized to the carbon level of soil, $K_{F\text{OC}}$, in the correlation with the different functional groups content. This normalized constant depends only on the specific characteristics of the soil organic matter, which differ considerably in the sorption capacity, due to differences in origin and genesis (10). Thus, alkyl, O,N-alkyl, aromatic, and carboxyl contents were correlated with $K_{F\text{OC}}$ (Table 3).

A strong positive correlation can be observed between carboxyl units and $K_{F\text{OC}}$ values. ^{13}C NMR spectroscopy of soil supplied with farmyard manure presented a higher relative area in the region usually attributed to carboxyl, amide, and ester functionalities, followed by soil fertilized with sewage sludge. The presence of a larger number of carboxyl units that can be responsible for the hydrogen bonding between atrazine and organic matter could be the explanation of the higher $K_{F\text{OC}}$ values obtained for these soils.

A positive correlation can also be observed for aromatic groups, although this correlation is not very high. It is important

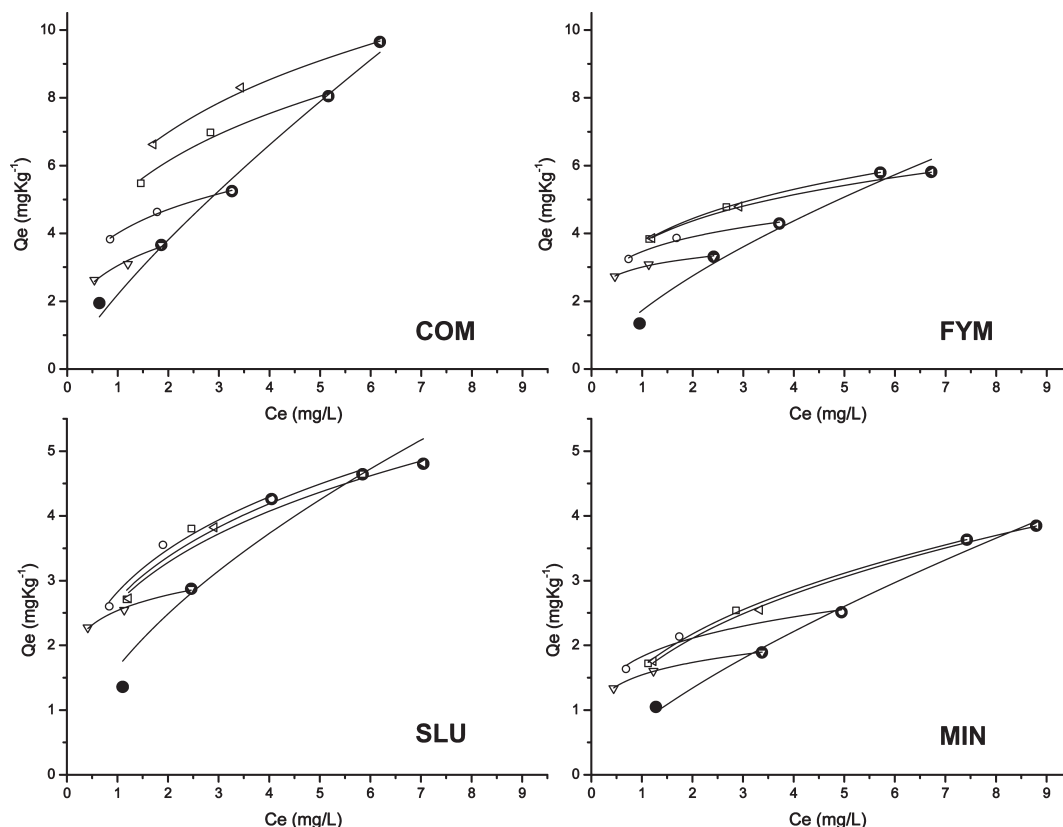


Figure 2. Freundlich sorption isotherms (solid symbol) and sequential desorption steps (open symbols) for atrazine in soils subjected to different fertilizations (MIN, mineral fertilizer; COM, compost fertilizer; FYM, farmyard manure; SLU, sewage sludge fertilizer).

to highlight the low organic carbon presented in the soil with mineral fertilization and the high noise observed in its ^{13}C NMR spectra, especially in that area (110–160 ppm). If we correlate the K_{FOC} with aromatic units, without using mineral fertilization the correlation improves tremendously, suggesting that higher aromatic compound contents induce higher K_{FOC} values. As presented in previous work (17), where the soil organic matter of the soils used was characterized by several techniques such as ^{13}C NMR and FTIR spectroscopy, the farmyard manure presented evidence of higher aromatic content. The more prevalent the aromatic content is, when compared to the hydrophilic (mostly polysaccharide), the greater the hydrophobicity of the humic substances. Thus, the obtained results could be an indication of hydrophobic interactions as a key role in binding of atrazine to organic matter (12).

A negative correlation was observed for alkyl and *O,N*-alkyl units. The soil supplied with mineral fertilizer and with compost presented higher alkyl units and lower carboxyl groups, decreasing the possibility of hydrogen bonding that could explain the lower K_{FOC} observed.

As indicated by the K_{FOC} values, the toxicity of atrazine applied to agricultural crops depends not only on the soil organic carbon content but also on the nature as well, because the bonding mechanism and the intensity depend greatly on the units of organic matter available for binding. Thus, the same application rate of atrazine to the soil, containing the same organic matter content, is expected to result in a lower environmental impact on the soil with farmyard manure, containing higher aromatic content, than in other soils with predominantly aliphatic structures. It is important to highlight that a compromise has to be reached between the content and nature of the organic matter applied to a specific soil.

The sorption isotherms for all of the soils in this study are nonlinear ($N < 1$), exhibiting values from 0.57, for soil fertilized with sewage sludge, to 0.79, for soil supplied with mineral fertilizer. Nonlinear sorption isotherms (convex curvature) are related with a modification of the affinity between the pesticide molecule and soils when the concentration increases (14). With an increase in the initial concentration of pesticide, the percentage adsorbed by the soil decreases, probably by a decrease in accessibility of free sorption sites (14).

Desorption Studies. Desorption isotherms describe the amount of the pesticide retained by the soil with pesticide concentration in the solution at equilibrium (Figure 2). Desorption is a key process affecting pesticide behavior in soils and controls the predisposition of a pesticide to be degraded and/or leached at different times (14). The Freundlich equation has reasonably described desorption of atrazine on the four soil samples used, with correlation coefficient values ranging from 0.963 to 1.000.

By comparison of K_{Fdes} (Table 4) obtained for the different soils, it is possible to conclude that higher values are obtained for the soil fertilized with compost, followed by farmyard manure and sewage sludge amended soil. Soil supplied with mineral fertilizer presented K_{Fdes} values significantly lower than those of the rest of the soils. Larger K_{Fdes} values indicate a greater proportion of the chemical retained by the soil (1). It was possible to establish a relationship between the K_{Fdes} and the organic matter content; higher organic matter content induces higher K_{Fdes} and, thus, lower desorption capacity.

As presented in the adsorption study, the K_{Fdes} can also be normalized to the carbon level of the soil, K_{FOCdes} , allowing us to verify the existence, or not, of an influence in desorption capacity due to the existence of differences on the organic matter properties, caused by differences in origin and genesis. The higher K_{FOCdes} values were obtained for the soil fertilized with farmyard

Table 4. Parameters of the Freundlich Equation Describing the Desorption Isotherms of Atrazine to the Four Soil Samples Used

soil ^a	initial concentration (mg/L)	K_{Fdes}^b	K_{FOCdes}^b	N_{des}^b	R^2	AHI ^b
MIN	4	1.54 (0.01)	1.24 (0.01)	0.17 (0.01)	0.999	0.234 (0.02)
	6	1.83 (0.08)	1.48 (0.06)	0.21 (0.04)	0.970	0.288 (0.06)
	9	1.66 (0.03)	1.34 (0.02)	0.39 (0.01)	0.999	0.540 (0.06)
	10	1.59 (0.04)	1.28 (0.03)	0.41 (0.02)	0.999	0.559 (0.06)
SLU	4	2.54 (0.02)	1.28 (0.01)	0.13 (0.01)	0.991	0.229 (0.04)
	6	2.82 (0.12)	1.42 (0.06)	0.30 (0.04)	0.983	0.527 (0.12)
	9	2.71 (0.24)	1.37 (0.12)	0.31 (0.06)	0.963	0.546 (0.15)
	10	2.64 (0.15)	1.33 (0.07)	0.31 (0.06)	0.987	0.542 (0.12)
FYM	4	3.00 (0.02)	2.04 (0.01)	0.12 (0.01)	0.989	0.177 (0.03)
	6	3.46 (0.07)	2.35 (0.05)	0.17 (0.01)	0.984	0.255 (0.05)
	9	3.72 (0.01)	2.53 (0.01)	0.25 (0.01)	1.000	0.382 (0.05)
	10	3.71 (0.02)	2.52 (0.01)	0.23 (0.01)	1.000	0.351 (0.05)
COM	4	3.05 (0.08)	1.10 (0.03)	0.27 (0.05)	0.970	0.341 (0.07)
	6	4.00 (0.05)	1.44 (0.02)	0.23 (0.01)	0.996	0.292 (0.03)
	9	5.00 (0.23)	1.80 (0.08)	0.30 (0.04)	0.986	0.372 (0.06)
	10	5.72 (0.17)	2.06 (0.06)	0.29 (0.02)	0.995	0.363 (0.04)

^a MIN, mineral fertilizer; SLU, sewage sludge fertilizer; FYM, farmyard manure; COM, compost fertilizer. ^b Standard deviation of the evaluated value is in parentheses.

manure, suggesting a higher quantity of atrazine retained by this type of soil fertilization. A higher aromatic content is usually considered not only to be responsible for a high sorption of organic compounds but also to contribute significantly to desorption hysteresis (15). Hysteresis is manifested by an increase in the difference between the adsorption and desorption isotherm slopes, which has been well documented (1, 11, 22, 23). Such differences in isotherms may be caused by several factors including different types of binding involved in atrazine sorption by soil organic matter, such as hydrogen bonds, charge transfer, ionic bonds, cation bridges, hydrophobic interactions, and physical diffusion into the humic substances (22). Boivin et al. (14) suggested the lack of similarity between adsorption and desorption due to hysteresis being probably a result of binding to organic matter and mineral particles, particularly clay minerals (24). By comparison of the AHI values it can be confirmed that the farmyard manure soil, with higher aromatic content and carboxyl units, is the one presenting lower AHI and, thus, higher desorption hysteresis. The aromatic content, responsible for the hydrophobicity of the organic matter, is involved in the hydrophobic interactions that are considered to be weak forces. However, the higher quantity of carboxyl units allows this type of organic matter to establish more hydrogen bonds than in the other soils' organic matter. Hydrogen bonds are stronger than hydrophobic interactions, and thus more difficult to break, which can be an explanation for the lower desorption capacity observed in the soil fertilized with farmyard manure.

For all soils we can generally observe an increase in AHI, and thus a decrease in hysteresis, with the amount of atrazine adsorbed. The trend of increasing desorption with increasing atrazine adsorbed can be explained by the existence of a limited number of sites available to establish stronger interactions. Therefore, most of these sites are occupied at low solute concentrations, whereas at high solute concentration more molecules are taken up by sites with the ability to establish weaker interactions and therefore can be readily desorbed (20).

In conclusion, the toxicity of atrazine applied to agricultural crops will depend not only on the content of organic carbon in the soil but also on its nature as well, because the bonding mechanism and its intensity depend greatly on the units of organic matter available for binding. The results of atrazine binding to organic matter pointed out that carboxyl- and aromatics-rich organic

matter are the most efficient binding agents for atrazine. The increase of aromatics-rich organic matter causes an increase in its hydrophobicity, thus increasing the hydrophobic interactions between atrazine and organic matter. The stronger interactions responsible for atrazine adsorption to organic matter are the hydrogen bonds due to the carboxyl units. Furthermore, the higher predominance of hydrogen bonds in adsorption of atrazine on soils will result in a decrease on desorption, because these are stronger binding forces than hydrophobic interactions and, thus, reduce the leaching of atrazine into drinking water resources and reduce runoff to rivers and other surface waters.

Farmyard manure can be effectively used to minimize the residual toxicity of atrazine-treated agricultural fields. The advantage of this type of traditional fertilization is its combined action as detoxifying agent and organic fertilizer. Thus, the same application rate of atrazine to the soil is expected to result in a lower environmental impact on the soil with farmyard manure, containing higher aromatic and carboxyl units, than in other soils with predominantly aliphatic structures. It is important to highlight that a compromise has to be reached between the content and nature of the organic matter applied to the soil.

LITERATURE CITED

- (1) Mersie, W.; Seybold, C. Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazine, and hydroxyatrazine on levy wetland soil. *J. Agric. Food Chem.* **1996**, *44*, 1925–1929.
- (2) Smith, M. C.; Shaw, D. R.; Massey, J. H.; Boyette, M.; Kingery, W. Using nonequilibrium thin-disc and batch equilibrium techniques to evaluate herbicide sorption. *J. Environ. Qual.* **2003**, *32*, 1393–1404.
- (3) Celano, G.; Šmejkalová, D.; Spaccini, R.; Piccolo, A. Interactions of three *s*-triazines with humic acids of different structure. *J. Agric. Food Chem.* **2008**, *57*, 7360–7366.
- (4) Ben-Hur, M.; Letey, J.; Farmer, W. J.; Williams, C. F.; Nelson, S. D. Soluble and solid organic matter effects in atrazine adsorption in cultivated soils. *Soil Sci. Soc. Am. J.* **2003**, *67*, 1140–1146.
- (5) Correia, F. V.; Macrae, A.; Guilherme, L. R. G.; Langenbach, T. Atrazine sorption and fate in a Ultisol from humid tropical Brazil. *Chemosphere* **2007**, *67*, 847–854.
- (6) Kovačios, I. D.; Parakeva, C. A.; Koutsoukos, P. G.; Payatakes, A. C. Adsorption of atrazine on soils: model study. *J. Colloid Interface Sci.* **2006**, *299*, 88–94.

- (7) Gao, J. P.; Maguhn, J.; Spitzauer, P.; Kettrup, A. Sorption of pesticides in the sediment of the Teufelsweiher pond (southern Germany) II: competitive adsorption, desorption of aged residues and effect of dissolved organic carbon. *Water Res.* **1998**, *32*, 2089–2094.
- (8) Lesan, H. M.; Bhandari, A. Atrazine sorption on surface soils: time-dependent phase distribution and apparent desorption hysteresis. *Water Res.* **2003**, *37*, 1644–1654.
- (9) Kah, M.; Brown, C. D. Changes in pesticide adsorption with time at high soil to solution ratios. *Chemosphere* **2007**, *68*, 1335–1343.
- (10) OECD. *Guideline TG 106. OECD Guideline for the Testing of Chemicals. Adsorption – Desorption using a Batch Equilibrium Method*; Organization for Economic Co-operation and Development: Paris, France, 2000.
- (11) Spark, K. M.; Swift, R. S. Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ.* **2002**, *298*, 147–161.
- (12) Kulikova, N. A.; Perminova, I. V. Binding of atrazine to humic substances from soil, peat, and coal related to their structure. *Environ. Sci. Technol.* **2002**, *36*, 3720–3724.
- (13) Nemeth-Konda, L.; Füleky, Gy.; Morovjan, Gy.; Csokan, P. Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. *Chemosphere* **2002**, *48*, 545–552.
- (14) Boivin, A.; Cherrier, R.; Schiavon, M. A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere* **2005**, *61*, 668–676.
- (15) Chefetz, B.; Bilkis, Y. I.; Polubesova, T. Sorption–desorption behaviour of atrazine and phenylurea herbicides in Kishon river sediments. *Water Res.* **2004**, *38*, 4383–4394.
- (16) Loganathan, V. A.; Feng, Y.; Sheng, G. D.; Clement, T. P. Crop-residue-derived char influences sorption, desorption and bioavailability of atrazine in soils. *Soil Biol. Biochem.* **2009**, *73*, 967–974.
- (17) Lima, D. L. D.; Santos, S. M.; Scherer, H. W.; Schneider, R. J.; Duarte, A. C.; Santos, E. B. H.; Esteves, V. I. Effects of organic and inorganic amendments on soil organic matter properties. *Geoderma* **2009**, *150*, 38–45.
- (18) Scherer, H. W.; Goldbach, H. E.; Clemens, J. Potassium dynamics in the soil and yield formation in a long-term field experiment. *Plant Soil Environ.* **2003**, *49*, 531–535.
- (19) Lima, D. L. D.; Erny, G. L.; Esteves, V. I. Application of MEKC to the monitoring of atrazine sorption behaviour on soils. *J. Sep. Sci.* **2009**, *32*, 4241–4246.
- (20) Drori, Y.; Aizenshtat, Z.; Chefetz, B. Sorption–desorption behaviour of atrazine in soils irrigated with reclaimed wastewater. *Soil Sci. Soc. Am. J.* **2005**, *69*, 1703–1710.
- (21) Singh, N.; Berns, A. E.; Hennecke, D.; Hoerner, J.; Koerdel, W.; Schaeffer, A. Effect of soil organic matter chemistry on sorption of trinitrotoluene and 2,4-dinitrotoluene. *J. Hazard. Mater.* **2010**, *173*, 343–348.
- (22) Prata, F.; Lavorenti, A.; Vanderborght, J.; Burauel, P.; Vereecken, H. Miscible displacement, sorption and desorption of atrazine in a Brazilian oxisol. *Vadose Zone J.* **2003**, *2*, 728–738.
- (23) Yang, W.; Zhang, J.; Zhang, C.; Zhu, L.; Chen, W. Sorption and resistant desorption of atrazine in typical Chinese soils. *J. Environ. Qual.* **2009**, *38*, 171–179.
- (24) Fruhstorfer, P.; Schneider, R.; Weil, L.; Niessner, R. Factors influencing the adsorption of atrazine on montmorillonitic and kaolinitic clays. *Sci. Total Environ.* **1993**, *138*, 317–328.

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